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(54) **SEGMENTED COPOLYMER COMPOSITIONS AND COATINGS INCORPORATING THESE COMPOSITIONS**

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See application file for complete search history.

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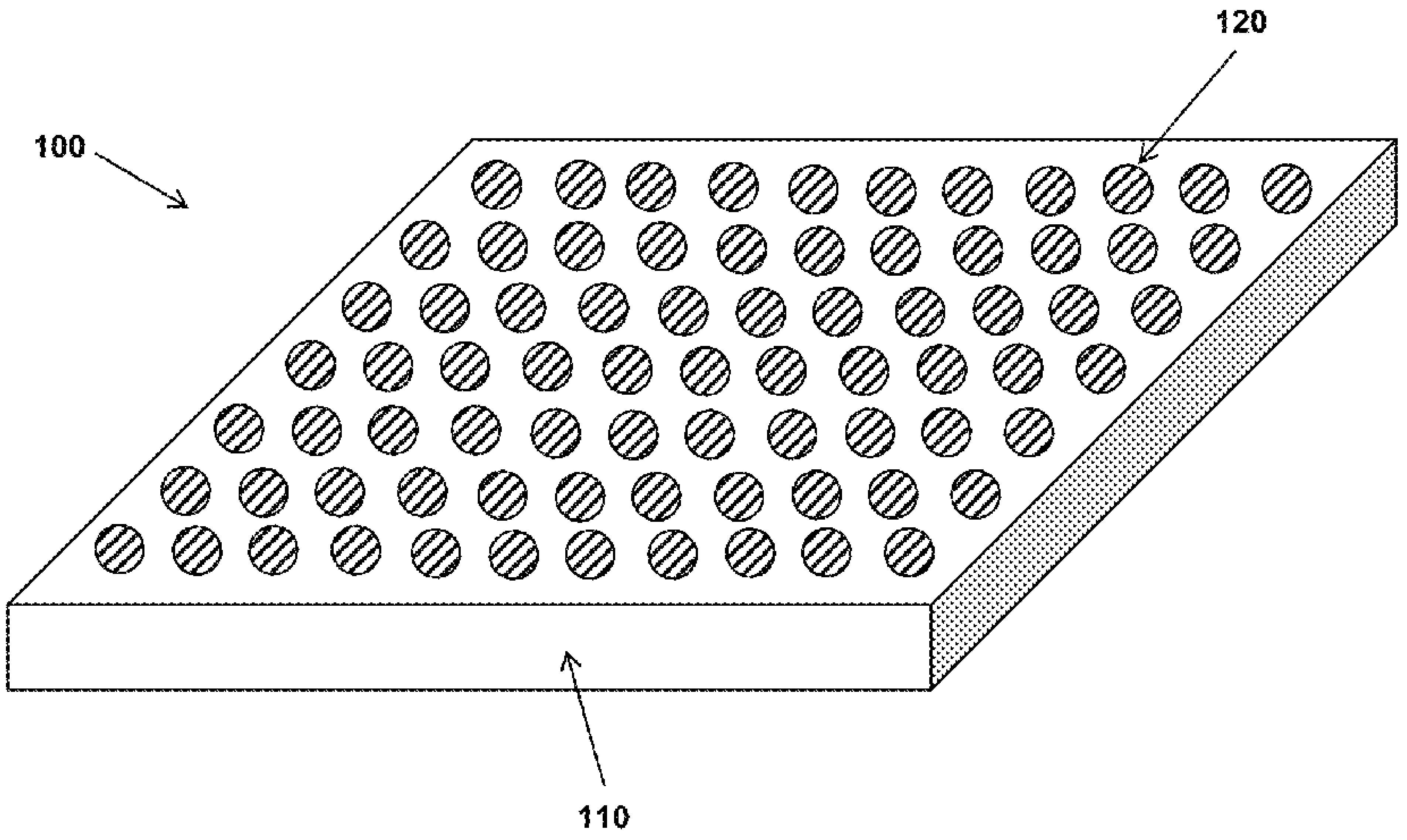
(57) **ABSTRACT**

Some variations provide a segmented copolymer composition comprising: fluoropolymer first soft segments that are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated; polyester or polyether second soft segments that are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated; isocyanate species possessing an isocyanate functionality of 2 or greater; and polyol or polyamine chain extenders or crosslinkers, wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0. Exemplary segmented copolymers are disclosed. The segmented copolymer composition may be present in a low-friction, low-adhesion coating. Such a coating may be characterized by a coefficient of friction, measured at 90% relative humidity, less than 0.7. Such a coating may be characterized by an average kinetic delay of surface ice formation of at least 10 minutes at −10° C. These coatings are useful as bugphobic and icephobic coatings.

11 Claims, 3 Drawing Sheets



Related U.S. Application Data

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(51) **Int. Cl.**

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C08G 81/02	(2006.01)
C09D 175/08	(2006.01)
C08G 18/38	(2006.01)

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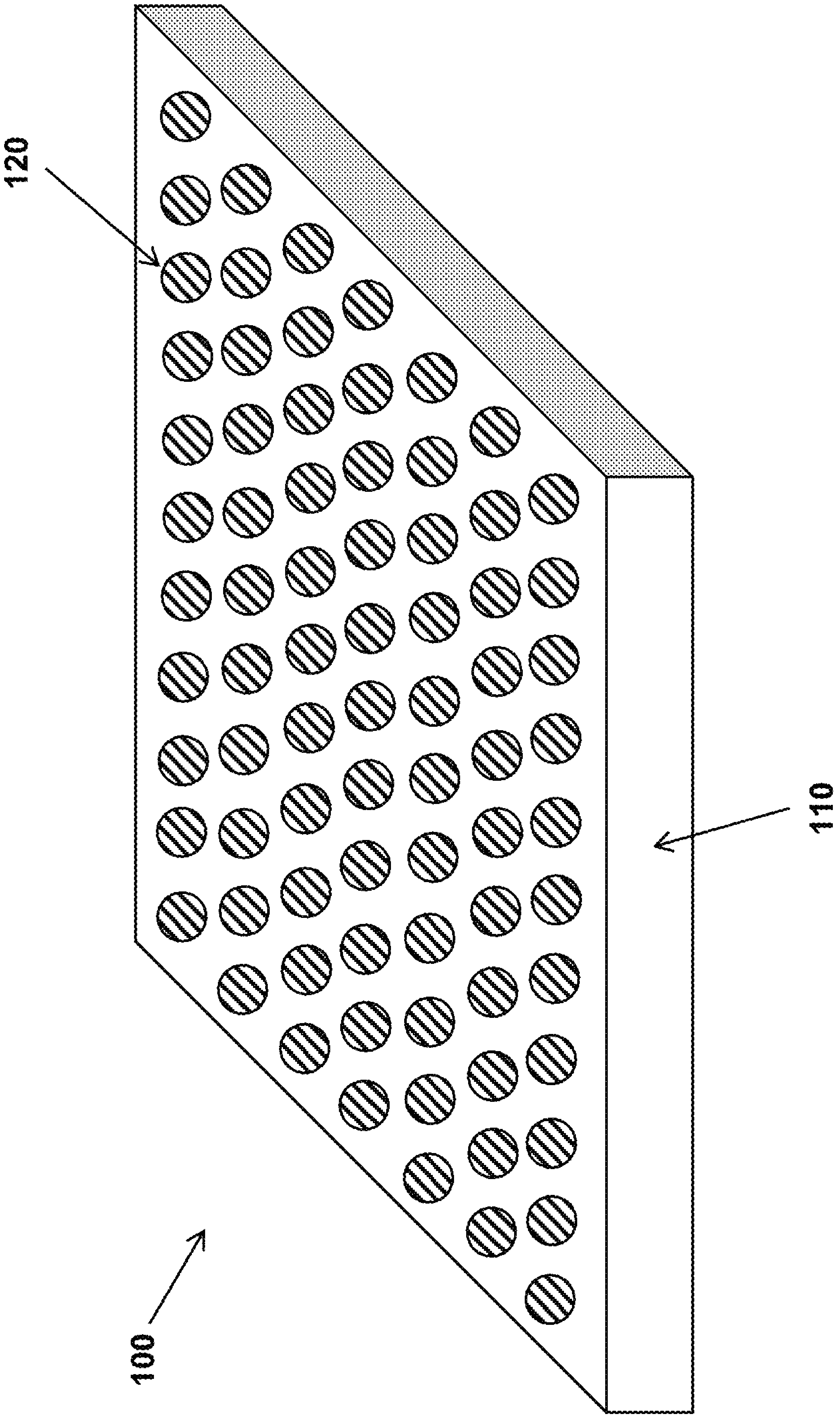


FIG. 1

FIG. 2

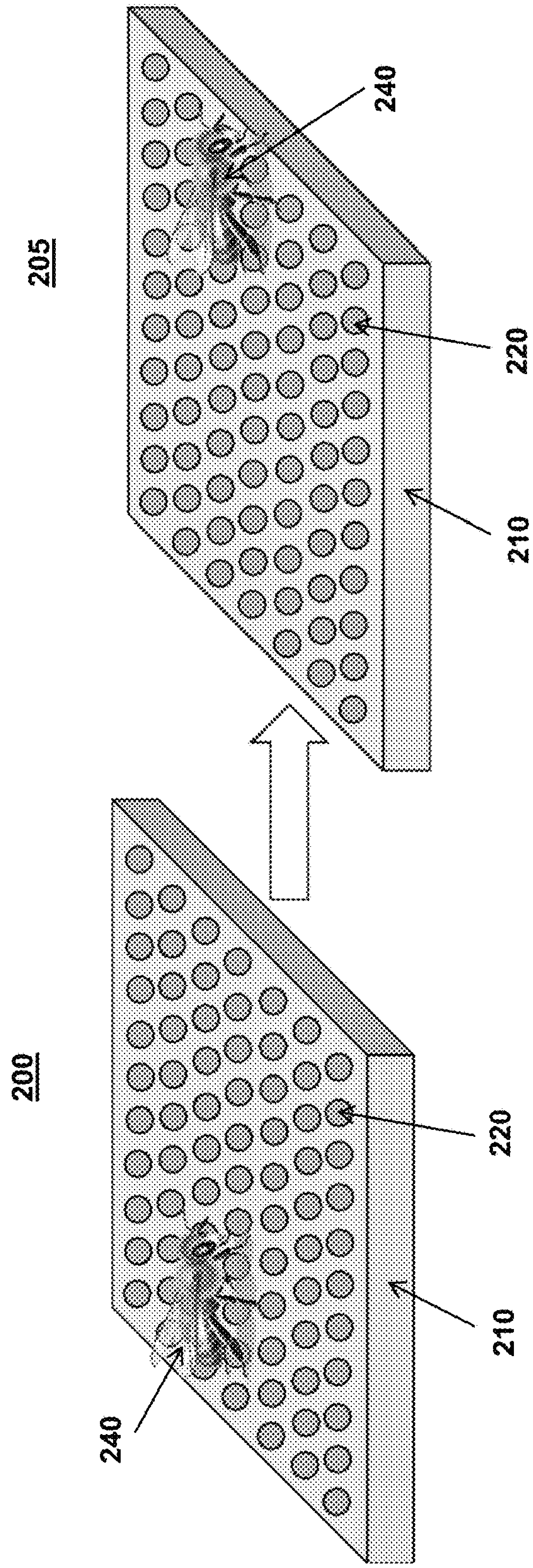


FIG. 3

Example	PEG:Fluoropolymer Molar Ratio	Coefficient of Friction at 40-55% Humidity	Coefficient of Friction at 85-90% Humidity	Freezing Delay on –10°C Surface
Al Control	–	–	–	0.2 ± 0.1 min
A	0	0.93	0.70	1.3 ± 0.9 min
B	1.0	0.36	0.48	11.5 ± 11.9 min
C	1.33	0.19	0.47	24.8 ± 2.6 min
D	1.0	0.34	0.48	30.2 ± 3.6 min
E	3.0	0.25	≥1.19 (Tacky)	6.2 ± 4.0 min
F	3.0	0.25	≥1.19 (Tacky)	2.8 ± 1.3 min

SEGMENTED COPOLYMER COMPOSITIONS AND COATINGS INCORPORATING THESE COMPOSITIONS

PRIORITY DATA

This patent application is a non-provisional application claiming priority to U.S. Provisional Patent App. No. 62/038,878, filed on Aug. 19, 2014, which is hereby incorporated by reference herein. This patent application is also a continuation-in-part of U.S. patent application Ser. No. 14/658,188, filed on Mar. 14, 2015, which is hereby incorporated by reference herein.

FIELD OF THE INVENTION

The present invention generally relates to low-friction and low-adhesion materials, coatings, and systems.

BACKGROUND OF THE INVENTION

Coatings and materials can become soiled from debris (particles, insects, oils, etc.) impacting the surface. The debris affects airflow over the surface as well as aesthetics and normally is removed by washing.

Many attempts are described to mitigate insect accumulation during the early days of aircraft development. These include mechanical scrapers, deflectors, traps, in-flight detachable surfaces, in-flight dissolvable surfaces, viscous surface fluids, continuous washing fluids, and suction slots. The results of most of these trials were determined ineffective or impractical for commercial use.

Recently, Wohl et al., "Evaluation of commercially available materials to mitigate insect residue adhesion on wing leading edge surfaces," *Progress in Organic Coatings* 76 (2013) 42-50 describe work at NASA to create anti-insect adhesion or "bugphobic" surfaces. Wohl et al. tested the effect of organic-based coatings on insect adhesion to surfaces, but the coatings did not fully mitigate the issue. Wohl et al. also describe previously used approaches to reduce bug adhesion such as mechanical scrapers, deflectors, paper and/or other coverings, elastic surfaces, soluble films, and washing the surface continually with fluid.

One approach to this problem is to create a self-cleaning surface that removes debris from itself by controlling chemical interactions between the debris and the surface.

Superhydrophobic and superoleophobic surfaces create very high contact angles (>150°) between the surface and drops of water and oil, respectively. The high contact angles result in the drops rolling off the surface rather than remaining on the surface. These surfaces do not repel solid foreign matter or vapors of contaminants. Once soiled by impact, debris will remain on the surface and render it ineffective. Also, these surfaces lose function if the nanostructured top surface is scratched.

Enzyme-filled coatings leech out enzymes that dissolve debris on the surface. However, the enzymes are quickly depleted and cannot be refilled, rendering this approach impractical.

Kok et al., "Influence of surface characteristics on insect residue adhesion to aircraft leading edge surfaces," *Progress in Organic Coatings* 76 (2013) 1567-1575, describe various polymer, sol-gel, and superhydrophobic coatings tested for reduced insect adhesion after impact. The best-performing materials were high-roughness, superhydrophobic surfaces. However, they did not show that debris could be removed from the superhydrophobic surfaces once insects broke on the surface.

Polymeric materials having low surface energies are widely used for non-stick coatings. These materials are tailored with careful control of their chemical composition (thus surface energy) and mechanical properties. Polymers containing low-energy perfluoropolyethers and perfluoroalkyl groups have been explored for low adhesion and solvent repellency applications. While these low-energy polymers facilitate release of materials adhering to them in both air and water, they do not necessarily prevent adhesion of foreign substances. See Vaidya and Chaudhury, "Synthesis and Surface Properties of Environmentally Responsive Segmented Polyurethanes," *Journal of Colloid and Interface Science* 249, 235-245 (2002). A fluorinated polyurethane is described in U.S. Pat. No. 5,332,798 issued Jul. 26, 1994 to Ferreri et al.

Fluoropolymer sheets or treated surfaces have low surface energies and thus low adhesion force between foreign matter and the surface. However, friction between impacting debris and the surface results in the sticking of contaminants.

Fluorofluid-filled surfaces have very low adhesion between impacting debris and the surface. However, if any of the fluid is lost, the surface cannot be refilled/renewed once applied on the vehicle, and thus loses its properties (see Wong et al., "Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity," *Nature* 477, 443-447, 2011).

In view of the shortcomings in the art, improved coating materials and material systems, and compositions suitable for these systems, are needed. Improved properties with respect to freezing delays and coefficients of friction are desired.

SUMMARY OF THE INVENTION

The present invention addresses the aforementioned needs in the art, as will now be summarized and then further described in detail below.

Some variations provide a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

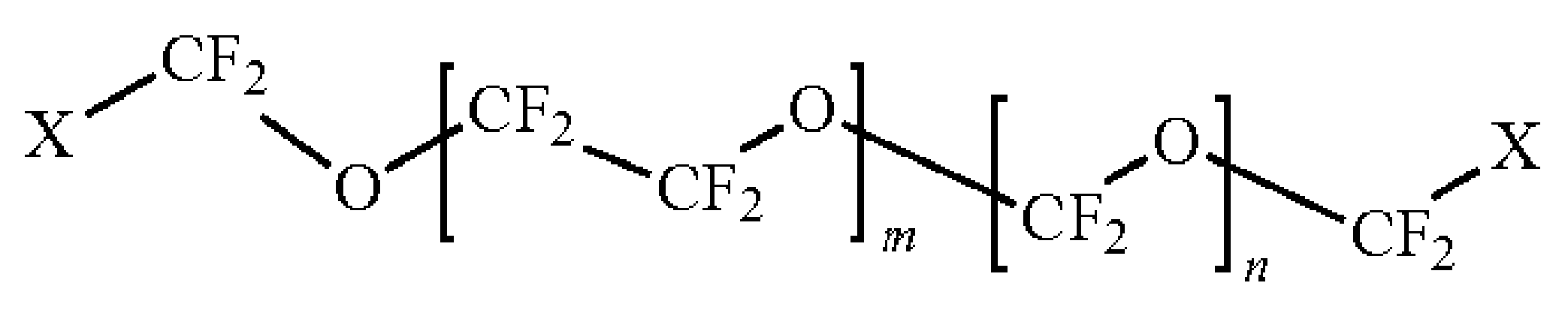
(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof, wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0.

In some embodiments, the molar ratio of the second soft segments to the first soft segments is from about 0.1 to about 1.5.

In some embodiments, the fluoropolymers are selected from the group consisting of polyfluoroethers, perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof. In certain embodiments, the fluoropolymers include a fluoropolymer having the structure:



wherein:

$X=CH_2—(CH_2—CH_2—O)_p—OH$ wherein p=0 to 50;
m=1 to 100; and
n=1 to 100.

In some embodiments, the polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), poly(propylene glycol) (also known as poly(propylene oxide)), poly(tetrahydrofuran), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly (hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof.

In some embodiments, the isocyanate species is selected from the group consisting of 4,4'-methylenebis(cyclohexyl isocyanate), hexamethylene diisocyanate, cycloalkyl-based diisocyanates, tolylene-2,4-diisocyanate, 4,4'-methylenebis (phenyl isocyanate), isophorone diisocyanate, and combinations or derivatives thereof.

The polyol or polyamine chain extender or crosslinker possesses a functionality of 2 or greater, in some embodiments. At least one polyol or polyamine chain extender or crosslinker may be selected from the group consisting of 1,3-butanediol,1,4-butanediol, 1,3-propanediol, 1,2-ethanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, neopentyl glycol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, ethanol amine, diethanol amine, methyldiethanolamine, phenyldiethanolamine, glycerol, trimethylolpropane, 1,2,6-hexanetriol, triethanolamine, pentaerythritol, ethylenediamine, 1,3-propanediamine, 1,4-buatendiamine, diethyltoluenediamine, dimethylthiotoluenediamine, isophoronediamine, diaminocyclohexane, N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine, and homologues, derivatives, or combinations thereof.

Following a suitable chemical reaction, the segmented copolymer composition contains, in a hard segment, the reacted form of the one or more isocyanate species, combined with the reacted form of the one or more polyol or polyamine chain extenders or crosslinkers. In some embodiments, the hard segment is present in an amount from about 5 wt % to about 60 wt %, based on total weight of the composition.

The segmented copolymer composition may be present in a coating, for example. Such a coating may be characterized by a contact angle of water on a coating surface of greater than 90°. Such a coating may be characterized by a coefficient of friction, measured at 90% relative humidity, less than 0.7. Such a coating may be characterized by an average kinetic delay of surface ice formation of at least 5 minutes at −10° C.

Some variations provide a low-friction, low-adhesion material (e.g., coating or bulk material) comprising:

a substantially continuous matrix containing a first component;

a plurality of inclusions containing a second component, wherein the inclusions are dispersed within the matrix;

wherein one of the first component or the second component is a low-surface-energy polymer having a surface energy between about 5 mJ/m^2 to about 50 mJ/m^2, and the other of the first component or the second component is a hygroscopic material,

and wherein the continuous matrix and the inclusions form a lubricating surface layer in the presence of humidity.

In some embodiments, the surface energy of the low-surface-energy polymer is between about 10 mJ/m^2 to about 40 mJ/m^2. In some preferred embodiments, the low-surface-energy polymer is a fluoropolymer selected from the group consisting of polyfluoroethers, perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof.

The hygroscopic material may be selected from the group consisting of poly(acrylic acid), poly(ethylene glycol), poly (2-hydroxyethyl methacrylate), poly(vinyl imidazole), poly (2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline), poly(vinylpyrolidone), cellulose, modified cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydrogels, PEG diacryalate, monoacrylate, and combinations thereof.

In some low-friction, low-adhesion materials, the low-surface-energy polymer and the hygroscopic material are covalently connected in a block copolymer. For example, the block copolymer may be a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

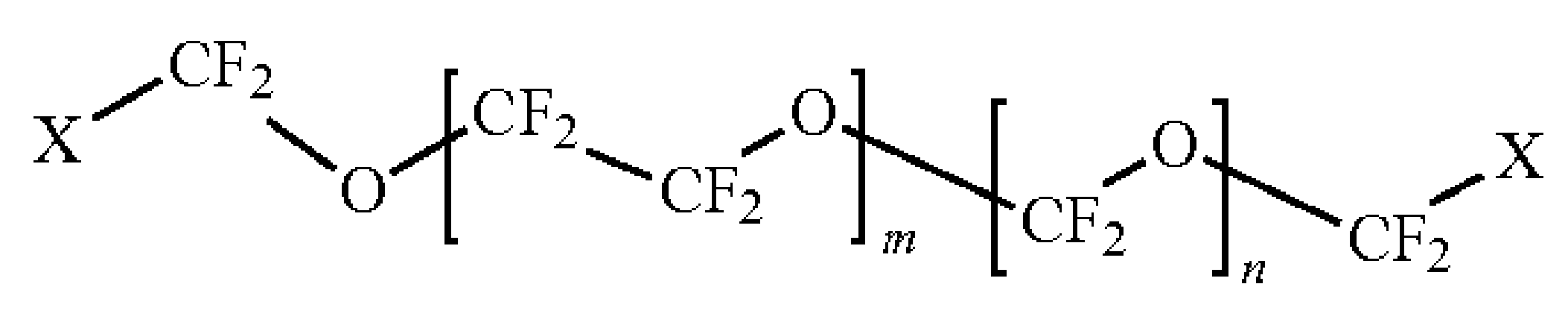
(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0, such as from about 0.1 to about 1.5.

In some embodiments, the fluoropolymers include a segmented copolymer based on fluoropolymer and poly(ethylene glycol), having the structure:



wherein:

$X=CH_2—(CH_2—CH_2—O)_p—OH$ wherein p=0 to 50;
m=1 to 100; and
n=1 to 100.

In some embodiments, the polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), polypropylene glycol), poly(tetrahydrofuran), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly(hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof.

The low-surface-energy polymer and/or the hygroscopic material may be surface-treated. The low-friction, low-adhesion material optionally further contains one or more additional components selected from the group consisting of a particulate filler, a pigment, a dye, a plasticizer, a flame retardant, a flattening agent, and a substrate adhesion promoter.

A particulate filler may be selected from the group consisting of silica, alumina, silicates, talc, aluminosilicates, barium sulfate, mica, diatomite, calcium carbonate, calcium sulfate, carbon, wollastonite, and combinations thereof.

Optionally, a particulate filler is surface-modified with a compound selected from the group consisting of fatty acids, silanes, alkylsilanes, fluoroalkylsilanes, silicones, alkyl phosphonates, alkyl phosphonic acids, alkyl carboxylates, alkyldisilazanes, and combinations thereof.

The low-friction, low-adhesion material may be characterized by a water absorption capacity of at least 10 wt % water based on total weight of the low-friction, low-adhesion material. The low-friction, low-adhesion material may be characterized by a surface contact angle of water of greater than 90°. The low-friction, low-adhesion material may be characterized by a coefficient of friction, measured at 90% relative humidity, less than 0.7. The low-friction, low-adhesion material may be characterized by an average delay in the formation of ice on a surface of the low-friction, low-adhesion material of at least 10 minutes at −10° C.

Variations of the invention also provide a precursor material for a low-friction, low-adhesion material, the precursor material comprising:

a hardenable material capable of forming a substantially continuous matrix containing a first component; and

a plurality of inclusions containing a second component, wherein the inclusions are dispersed within the hardenable material,

wherein one of the first component or the second component is a low-surface-energy polymer having a surface energy between about 5 mJ/m^2 to about 50 mJ/m^2, and the other of the first component or the second component is a hygroscopic material.

In some embodiments, the surface energy of the low-surface-energy polymer is between about 10 mJ/m^2 to about 40 mJ/m^2. In some embodiments, the low-surface-energy polymer is a fluoropolymer, such as one selected from the group consisting of polyfluoroethers, perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof.

In some embodiments, the hygroscopic material is selected from the group consisting of poly(acrylic acid), poly(ethylene glycol), poly(2-hydroxyethyl methacrylate), poly(vinyl imidazole), poly(2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline), poly(vinylpyrolidone), cellulose, modified cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydrogels, PEG diacryalate, monoacrylate, and combinations thereof.

The low-surface-energy polymer and the hygroscopic material may be covalently connected, or are capable of being covalently connected, in a block copolymer. For example, a block copolymer may be a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

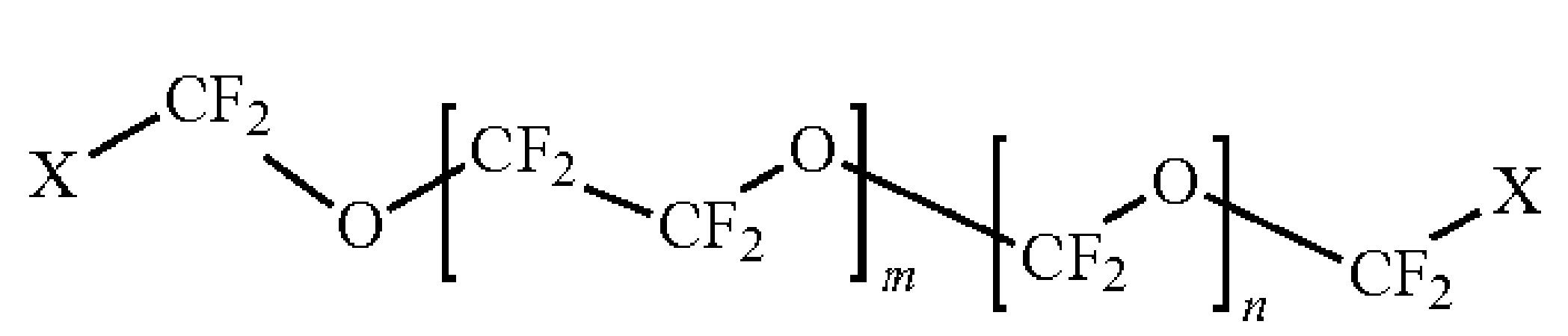
(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0, such as from about 0.1 to about 1.5.

In some embodiments, the fluoropolymers include a fluoropolymer having the structure:



wherein:

$X=CH_2-(CH_2-CH_2-O)_p-OH$ wherein p=0 to 50;

m=1 to 100; and

n=1 to 100.

In some embodiments, the polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), poly(propylene glycol) (also known as poly(propylene oxide)), poly(tetrahydrofuran), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly(hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof.

The low-surface-energy polymer and/or the hygroscopic material may be surface-treated, either prior to introduction into the precursor material or prior to conversion of the precursor material to the low-friction, low-adhesion material.

The precursor material may further contain one or more additional components selected from the group consisting of a particulate filler, a pigment, a dye, a plasticizer, and a flame retardant. Alternatively, or additionally, such additional components may be introduced during the conversion of the precursor material to the low-friction, low-adhesion material, or to the low-friction, low-adhesion material after it is formed.

Specific particulate fillers include, for example, silica, alumina, silicates, talc, aluminosilicates, barium sulfate, mica, diatomite, calcium carbonate, calcium sulfate, carbon, wollastonite, and combinations thereof. The particulate fillers may be surface-modified with a compound selected from the group consisting of fatty acids, silanes, silicones, alkyl phosphonates, alkyl phosphonic acids, alkyl carboxylates, and combinations thereof. Optionally, the fillers may be surface-modified with a hydrophobic material, such as (but not limited to) an alkylsilane, a fluoroalkylsilane, and/or an alkyldisilazane (e.g., hexamethyldisilazane).

In some variations of the invention, a material or coating precursor is applied to a substrate (such as a surface of an automobile or aircraft) and allowed to react, cure, or harden to form a final coating, wherein the material, coating precursor, or final coating contains a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** depicts the structure of some variations of the invention, providing a low-friction, low-adhesion material.

FIG. **2** illustrates the mode of action according to some variations, showing an insect sliding off the surface following impact.

FIG. **3** includes a table of experimental data from Examples A, B, C, D, E, and F described herein.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The materials, compositions, structures, systems, and methods of the present invention will be described in detail by reference to various non-limiting embodiments.

This description will enable one skilled in the art to make and use the invention, and it describes several embodiments, adaptations, variations, alternatives, and uses of the invention. These and other embodiments, features, and advantages of the present invention will become more apparent to those skilled in the art when taken with reference to the following detailed description of the invention in conjunction with the accompanying drawings.

As used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly indicates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art to which this invention belongs.

Unless otherwise indicated, all numbers expressing conditions, concentrations, dimensions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending at least upon a specific analytical technique.

The term “comprising,” which is synonymous with “including,” “containing,” or “characterized by” is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. “Comprising” is a term of art used in claim language which means that the named claim elements are essential, but other claim elements may be added and still form a construct within the scope of the claim.

As used herein, the phase “consisting of” excludes any element, step, or ingredient not specified in the claim. When the phrase “consists of” (or variations thereof) appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole. As used herein, the phase “consisting essentially of” limits the scope of a claim to the specified elements or method steps, plus those that do not materially affect the basis and novel characteristic(s) of the claimed subject matter.

With respect to the terms “comprising,” “consisting of,” and “consisting essentially of,” where one of these three terms is used herein, the presently disclosed and claimed subject matter may include the use of either of the other two terms. Thus in some embodiments not otherwise explicitly recited, any instance of “comprising” may be replaced by “consisting of” or, alternatively, by “consisting essentially of.”

Some variations of this invention are premised on the discovery of a material that possesses both low surface energy (for low adhesion) and the ability to absorb water. A structured material or coating, as disclosed, passively absorbs water from the atmosphere and then expels this water upon impact with the impacting debris, to create a lubrication/self-cleaning layer and reduce the friction and adhesion of the impacting body (such as an insect) on the surface. The material may be used as a coating or as a surface.

The coating in some embodiments may be characterized as “bugphobic,” which is intended to mean the coating has relatively low adhesion with an impacting bug. Because these materials trap a layer of water near the surface, they also can delay the formation of ice, in some embodiments. The coating in some embodiments may be characterized as “icephobic,” which is intended to mean the coating is capable of delaying the formation of ice and/or causing a freezing-point depression of ice, compared to a bare substrate. The lubricating component has the ability to trap and organize a layer of water at the surface to both inhibit freezing and reduce adhesion forces in ice that does begin to accumulate on the surface.

In contrast to prior structures and methods, the disclosed material can absorb water from the air and use this water as a lubricant to wash and remove debris from the surface. The surface contains domains of a low-surface-energy polymer (such as, but not limited to, a fluoropolymer) providing low adhesion, and domains of a hygroscopic material. Without being limited by theory, it is speculated that in some embodiments, the hygroscopic material absorbs water and releases some of it back onto the surface during impact. The atmospheric water is thus captured as a lubricant and is a continually available, renewable resource.

By reducing friction, the debris is less likely to embed in or otherwise attach to the surface and instead will slough off the surface (as illustrated in FIG. **2**, where debris is depicted as a wasp). Debris may be organic or inorganic and may include insects, dirt, dust, soot, ash, pollutants, particulates, ice, seeds, plant or animal fragments, plant or animal waste products, combinations or derivatives of any of the foregoing, and so on.

The domains of hygroscopic material exist throughout the material, in both planar and depth dimensions. The anti-adhesion function is retained even after abrasion of the top layer of the material.

In some variations, low-friction and low-adhesion structures are created by a heterogeneous microstructure comprising a low-surface-energy polymer that is interspersed with hygroscopic domains (lubricating inclusions). Debris impacting the surface has low adhesion energy with the surface, due to the presence of the low-surface-energy polymer, and the debris will not remain on the surface.

Preferred embodiments employ fluoropolymers, without limitation of the invention, as described in more detail below. A preferred technique to compatiblize fluoropolymers and hygroscopic materials is the use of segmented polyurethane or urea systems. These species demonstrate strong hydrogen bonding potential between them and as a result can create strong associative forces between the chains. In order to produce elastomeric materials, regions of highly flexible and weakly interacting chains (soft segments) must be incorporated with strongly associating elements (hard segments) and this can be provided in a segmented copolymerization scheme. Segmented copolymers provide a straightforward synthetic route toward block architectures using segments with vastly differing properties. Such synthesis results in chains that possess alternating hard and soft segments composed of regions of high urethane bond density and the chosen soft segment component (e.g., fluoropolymer or hygroscopic element), respectively. This covalent linkage of dissimilar hard and soft blocks drives the systems to microphase separation and creates regions of flexible soft blocks surrounding regions of hard blocks. The associative forces among the hard segments prevent flow under stress and can produce elastomeric materials capable of displaying high elongation and tensile strength.

In a specific embodiment of the disclosure, there is provided a segmented copolymer composition. The composition comprises one or more α,ω (alpha, omega)-amine-terminated or α,ω (alpha, omega)-hydroxyl-terminated polyfluoropolymer first soft segments having an average molecular weight of between about 500 grams per mole to about 10,000 grams per mole. The exemplary composition further comprises one or more polyethylene glycol second soft segments having an average molecular weight of between about 500 grams per mole to about 10,000 grams per mole. A total content of the one or more first soft segments and the one or more second soft segments is present in an amount of from about 40% by weight to about 90% by weight, based on a total weight percent of the composition. The composition further comprises one or more hard segments present in an amount of from about 15% by weight to about 50% by weight, based on the total weight percent of the composition. The one or more hard segments comprise a combination of one or more isocyanate species and one or more low-molecular-weight polyol or polyamine chain extenders or crosslinkers. Preferred compositions are characterized a contact angle of water on the surface >90° and by a delay in the formation of ice on the surface.

Some variations provide a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0.

It is noted that (α,ω)-terminated polymers are terminated at each end of the polymer. The α-termination may be the same or different than the ω-termination. Also it is noted that in this disclosure, "(α,ω)-termination" includes branching at the ends, so that the number of terminations may be greater than 2 per polymer molecule. The polymers herein may be linear or branched, and there may be various terminations and functional groups within the polymer chain, besides the end (α,ω) terminations.

In some embodiments, the molar ratio of the second soft segments to the first soft segments is from about 0.1 to about 1.5. In various embodiments, the molar ratio of the second soft segments to the first soft segments is about 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 1.95.

In this description, "polyurethane" is a polymer comprising a chain of organic units joined by carbamate (urethane) links, where "urethane" refers to N(H)—(C═O)—O—. Polyurethanes are generally produced by reacting an isocyanate containing two or more isocyanate groups per molecule with one or more polyols containing on average two or more hydroxyl groups per molecule, in the presence of a catalyst.

Polyols are polymers in their own right and have on average two or more hydroxyl groups per molecule. For example, α,ω-hydroxyl-terminated perfluoropolyether is a type of polyol.

"Isocyanate" is the functional group with the formula —N═C═O. For the purposes of this disclosure, S—C(═O)—N(H)—R is considered a derivative of isocyanate.

"Polyfluoroether" refers to a class of polymers that contain an ether group—an oxygen atom connected to two alkyl or aryl groups, where at least one hydrogen atom is replaced by a fluorine atom in an alkyl or aryl group.

"Perfluoropolyether" (PFPE) is a highly fluorinated subset of polyfluoroethers, wherein all hydrogen atoms are replaced by fluorine atoms in the alkyl or aryl groups.

"Polyurea" is a polymer comprising a chain of organic units joined by urea links, where "urea" refers to N(H)—(C═O)—N(H)—. Polyureas are generally produced by reacting an isocyanate containing two or more isocyanate groups per molecule with one or more multifunctional amines (e.g., diamines) containing on average two or more amine groups per molecule, in the presence of a catalyst.

A "chain extender or crosslinker" is a compound (or mixture of compounds) that link long molecules together and thereby complete a polymer reaction. Chain extenders or crosslinkers are also known as curing agents, curatives, or hardeners. In polyurethane/urea systems, a curative is typically comprised of hydroxyl-terminated or amine-terminated compounds which react with isocyanate groups present in the mixture. Diols as curatives form urethane linkages, while diamines as curatives form urea linkages. The choice of chain extender or crosslinker may be determined by end groups present on a given prepolymer. In the case of isocyanate end groups, curing can be accomplished through chain extension using multifunctional amines or alcohols, for example. Chain extenders or crosslinkers can have an average functionality greater than 2 (such as 3 or greater), i.e. beyond diols or diamines.

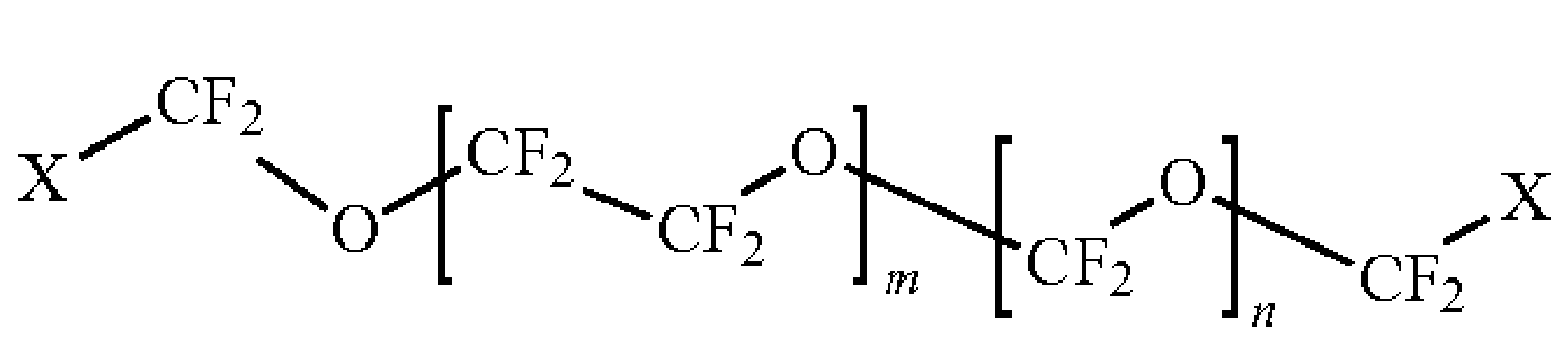
The one or more chain extenders or crosslinkers (or reaction products thereof) may be present in a concentration, in the segmented copolymer composition, from about 0.01 wt % to about 10 wt %, such as about 0.05 wt % to about 1 wt %.

As meant herein, a "low-surface-energy polymer" means a polymer, or a polymer-containing material, with a surface energy of no greater than 50 mJ/m^2. The principles of the invention may be applied to low-surface-energy materials with a surface energy of no greater than 50 mJ/m^2, in general (i.e., not necessarily limited to polymers).

In some embodiments, the low-surface-energy polymer includes a fluoropolymer, such as (but not limited to) a fluoropolymer selected from the group consisting of polyfluoroethers, perfluoropolyethers, fluoroacrylates, fluorosilicones, and combinations thereof.

In these or other embodiments, the low-surface-energy polymer includes a siloxane. A siloxane contains at least one Si—O—Si linkage. The low-surface-energy polymer may consist of polymerized siloxanes or polysiloxanes (also known as silicones). One example is polydimethylsiloxane.

In some embodiments, the fluoropolymers are selected from the group consisting of perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof. In certain embodiments, the fluoropolymers include a fluoropolymer segmented copolymer with poly(ethylene glycol) having the structure:



wherein:

$X=CH_2—(CH_2—CH_2—O)_p—OH$ wherein p=0 to 50;

m=1 to 100; and

n=1 to 100.

In some embodiments, the polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), poly(propylene glycol), poly(tetrahydrofuran), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly(hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof.

In some embodiments, the isocyanate species is selected from the group consisting of 4,4'-methylenebis(cyclohexyl isocyanate), hexamethylene diisocyanate, cycloalkyl-based diisocyanates, tolylene-2,4-diisocyanate, 4,4'-methylenebis (phenyl isocyanate), isophorone diisocyanate, and combinations or derivatives thereof.

The polyol or polyamine chain extender possesses a functionality of 2 or greater, in some embodiments. At least one polyol or polyamine chain extender may be selected from the group consisting of 1,4-butanediol, 1,3-propanediol, 1,2-ethanediol, glycerol, trimethylolpropane, ethylenediamine, isophoronediamine, diaminocyclohexane, and homologues, derivatives, or combinations thereof.

Following a suitable chemical reaction, the segmented copolymer composition contains, in a hard segment, the reacted form of the one or more isocyanate species, combined with the reacted form of the one or more polyol or polyamine chain extenders or crosslinkers. In some embodiments, the hard segment is present in an amount from about 5 wt % to about 60 wt %, based on total weight of the composition.

The segmented copolymer composition may be present in a coating, for example. Such a coating may be characterized by a contact angle of water on a coating surface of greater than 90°. Such a coating may be characterized by an average kinetic delay of surface ice formation of at least 5 minutes at −10° C.

The structure of some variations of the invention is shown in FIG. **1**. FIG. **1** depicts the structure of a coating or surface with low-friction and self-cleaning properties.

The structure **100** of FIG. **1** includes a continuous matrix **110**. A "continuous matrix" (or equivalently, "substantially continuous matrix") means that the matrix material is present in a form that includes chemical bonds among molecules of the matrix material. An example of such chemical bonds is crosslinking bonds between polymer chains. In a substantially continuous matrix **110**, there may be present various defects, cracks, broken bonds, impurities, additives, and so on. The structure **100** further includes a plurality of inclusions **120**, dispersed within the matrix **110**, each of the inclusions **120** comprising a hygroscopic material.

Optionally, the continuous matrix **110** may further comprise one or more additives selected from the group consisting of fillers, colorants, UV absorbers, defoamers, plasticizers, viscosity modifiers, density modifiers, catalysts, and scavengers.

The mode of action according to some variations is shown in FIG. **2**. The structure of FIG. **2** includes a continuous matrix **210** and a plurality of inclusions **220**. FIG. **2** illustrates the response of the surface **200** to an impact of debris, which in this illustration is a bug **240** (e.g, wasp), as a non-limiting example. The bug **240** slides across the surface (**200/205**) instead of breaking apart, ultimately leaving the surface **205** and thereby not leaving behind debris bound to the material.

Some variations provide a low-friction, low-adhesion material (e.g., coating or bulk material) comprising:

a substantially continuous matrix containing a first component;

a plurality of inclusions containing a second component, wherein the inclusions are dispersed within the matrix;

wherein one of the first component or the second component is a low-surface-energy polymer having a surface energy between about 5 mJ/m^2 to about 50 mJ/m^2, and the other of the first component or the second component is a hygroscopic material,

and wherein the continuous matrix and the inclusions form a lubricating surface layer in the presence of humidity.

In some embodiments, the surface energy of the low-surface-energy polymer is between about 10 mJ/m^2 to about 40 mJ/m^2, such as about 10, 15, 20, 25, 30, 35, or 40, mJ/m^2. In some preferred embodiments, the low-surface-energy polymer is a fluoropolymer selected from the group consisting of polyfluoroethers, perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof.

The hygroscopic material may be selected from the group consisting of poly(acrylic acid), poly(ethylene glycol), poly (2-hydroxyethyl methacrylate), poly(vinyl imidazole), poly (2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline), poly(vinylpyrolidone), cellulose, modified cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydrogels, PEG diacryalate, monoacrylate, and combinations thereof.

In certain embodiments, the hygroscopic material is also classified as a hydrophilic material. A hygroscopic substance will actively attract and absorb water. A hydrophilic substance is one where water will preferentially wet the surface, demonstrated by contact angles <90°.

The low-surface-energy polymer and the hygroscopic material may be phase-separated, i.e. they do not form a single continuous phase. There may be, but is not necessarily, some degree of chemical and/or physical bonding between the low-surface-energy polymer and the hygroscopic material.

The inclusions are three-dimensional objects or domains, which may be of any shape, geometry, or aspect ratio. In a three-dimensional object, an aspect ratio of exactly 1.0 means that all three characteristic length scales are identical, such as in a perfect cube. The aspect ratio of a perfect sphere is also 1.0. The inclusions may be geometrically symmetric or asymmetric. Randomly shaped asymmetric templates are, generally speaking, geometrically asymmetric. In some embodiments, inclusions are geometrically symmetric. Examples include cylinders, cones, rectangular prisms, pyramids, or three-dimensional stars.

In some embodiments, the inclusions are anisotropic. As meant herein, "anisotropic" inclusions have at least one chemical or physical property that is directionally dependent. When measured along different axes, an anisotropic inclusion will have some variation in a measurable property. The property may be physical (e.g., geometrical) or chemical in nature, or both.

The inclusions may be characterized as templates, domains, or regions (such as phase-separated regions). The inclusions are not a single, continuous framework in the coating. Rather, the inclusions are discrete, non-continuous and dispersed in the continuous matrix. The hygroscopic inclusions may be dispersed uniformly within the continuous matrix. In some low-friction, low-adhesion materials, the low-surface-energy polymer and the hygroscopic material are covalently connected in a block copolymer, in which the inclusions and the continuous matrix are distinct phases of the block copolymer.

As intended herein, a "block copolymer" means a copolymer containing a linear arrangement of blocks, where each block is defined as a portion of a polymer molecule in which the monomeric units have at least one constitutional or configurational feature absent from the adjacent portions. Several types of block copolymers are generally possible, including AB block copolymers, ABA block copolymers, ABC block copolymers, segmented block copolymers, and random copolymers. Segmented block copolymers are preferred, in some embodiments of the invention.

For example, a block copolymer may be a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

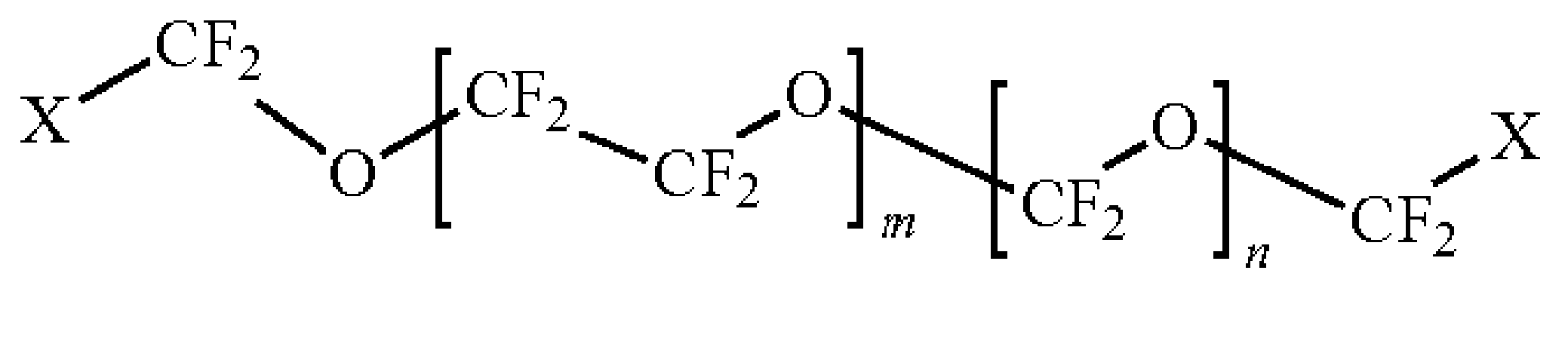
(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0, such as from about 0.1 to about 1.5.

In some embodiments, the fluoropolymers include a fluoropolymer having the structure:



wherein:

$X=CH_2—(CH_2—CH_2—O)_p—OH$ wherein p=0 to 50;

m=1 to 100; and

n=1 to 100.

In some embodiments, the polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), poly(propylene glycol), poly(tetrahydrofuran), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly(hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof.

A wide range of concentrations of components may be present in the low-friction, low-adhesion material. For example, the continuous matrix may be from about 5 wt % to about 95 wt %, such as from about 10 wt % to about 50 wt % of the material. The inclusions may be from about 1 wt % to about 90 wt %, such as from about 10 wt % to about 50 wt % of the coating.

Within the component containing the low-surface-energy polymer, the low-surface-energy polymer may be from about 50 wt % to 100 wt %, such as about 60, 70, 80, 90, 95, or 100 wt %. Within the component containing the hygroscopic material, the hygroscopic material may be from about 50 wt % to 100 wt %, such as about 60, 70, 80, 90, 95, or 100 wt %.

The low-surface-energy polymer and/or the hygroscopic material may be surface-treated, such as to adjust hydrophobicity. The low-friction, low-adhesion material optionally further contains one or more additional components selected from the group consisting of a particulate filler, a pigment, a dye, a plasticizer, a flame retardant, a flattening agent, and a substrate adhesion promoter.

A particulate filler may be selected from the group consisting of silica, alumina, silicates, talc, aluminosilicates, barium sulfate, mica, diatomite, calcium carbonate, calcium sulfate, carbon, wollastonite, and combinations thereof. The particulate fillers generally should be in the size range of about 5 nm to about 2 μm, such as about 20 nm to 100 nm.

The particulate fillers may be surface-modified with a compound selected from the group consisting of fatty acids, silanes, silicones, alkyl phosphonates, alkyl phosphonic acids, alkyl carboxylates, and combinations thereof. Optionally, the fillers may be surface-modified with a hydrophobic material, such as (but not limited to) an alkylsilane, a fluoroalkylsilane, and/or an alkyldisilazane (e.g., hexamethyldisilazane).

In some embodiments, the low-friction, low-adhesion material further includes voids. As intended herein, a "void" is a discrete region of empty space, or space filled with air or another gas, that is enclosed within the continuous matrix. The voids may be open (e.g., interconnected voids) or closed (isolated within the continuous matrix), or a combination thereof. The voids may partially surround inclusions.

The low-friction, low-adhesion material may be characterized by a water absorption capacity of at least 10 wt % water based on total weight of the low-friction, low-adhesion material. The material is characterized, according to some embodiments, by a water absorption capacity of at least 1, 2, 3, 4, 5, 6, 7, 8, or 9 wt % water, preferably at least 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt % water, based on total weight of the material.

The low-friction, low-adhesion material may be characterized by a surface contact angle of water of greater than 90° (hydrophobic). The material may also be hydrophilic, i.e. characterized by an effective contact angle of water that is less than 90°. In various embodiments, the material is characterized by an effective contact angle of water of about 70°, 75°, 80°, 85°, 90°, 95°, 100°, or higher.

The material may also be lipophobic or partially lipophobic in some embodiments. In various embodiments, the material is characterized by an effective contact angle of hexadecane (as a measure of lipophobicity) of about 50°, 55°, 60°, 65°, 70°, 75°, 80°, 85°, 90°, or higher.

The material may simultaneously have hydrophobic and lipophobic properties. In certain embodiments, the material is characterized by an effective contact angle of water of at least 90° (such as about 95-100°) and simultaneously an effective contact angle of hexadecane of at least 60° (such as about 65°). In certain embodiments, the material is characterized by an effective contact angle of water of at least 80°

(such as about 80-85°) and simultaneously an effective contact angle of hexadecane of at least 70° (such as about 75-80°).

In some embodiments, the material is characterized by a coefficient of friction, measured at 40-55% (e.g. 50%) relative humidity and room temperature, less than 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, or 0.3. In these or other embodiments, the material is characterized by a coefficient of friction, measured at 85% relative humidity and room temperature, less than 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, or 0.2. The low-friction, low-adhesion material may be characterized by a coefficient of friction, measured at 90% relative humidity, less than 0.7.

The coefficient of friction is relatively low due to the presence of a lubricating surface layer. By a "lubricating surface layer in the presence of humidity," it is meant a layer, multiple layers, a partial layer, or an amount of substance that lubricates the substrate such that it has a lower coefficient of friction compared to the substrate without the material present, when in the presence of some amount of atmospheric humidity.

The specific level of humidity is not regarded as critical, but in general may range from about 1% to 100%, typically about 30% to about 70% relative humidity. Relative humidity is the ratio of the water vapor density (mass per unit volume) to the saturation water vapor density. Relative humidity is also approximately the ratio of the actual to the saturation vapor pressure.

The substance that lubricates the substrate is primarily water, but it should be noted that other components from the environment may be present in the lubricating surface layer, including oils, metals, dust, dissolved gases, dissolved aqueous components, suspended non-aqueous components, fragments of debris, fragments of polymers, and so on.

The material may be characterized by a delay in the formation of ice on a surface of the material. For example, when a material surface is held at −10° C., the material provided by the invention may be characterized by an average delay in the formation of ice on the surface of at least about 10, 15, 20, 25, 30 minutes, or more.

In various embodiments, the material is a coating and/or is present at a surface of an object or region. The material may be utilized in relatively small applications, such as lens coatings, or for large structures, such as aircraft wings. In principle, the material could be present within a bulk region of an object or part, or could contain a temporary, protective laminating film for storage or transport, which is later removed to adhere to the vehicle, for example.

Variations of the invention also provide a precursor material for a low-friction, low-adhesion material, the precursor material comprising:

a hardenable material capable of forming a substantially continuous matrix containing a first component; and

a plurality of inclusions containing a second component, wherein the inclusions are dispersed within the hardenable material,

wherein one of the first component or the second component is a low-surface-energy polymer having a surface energy between about 5 mJ/m^2 to about 50 mJ/m^2, and the other of the first component or the second component is a hygroscopic material.

In some embodiments, the surface energy of the low-surface-energy polymer is between about 10 mJ/m^2 to about 40 mJ/m^2, such as about 10, 15, 20, 25, 30, 35, or 40, mJ/m^2. In some embodiments, the low-surface-energy polymer is a fluoropolymer, such as one selected from the group consisting of polyfluoroethers, perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof.

In some embodiments, the hygroscopic material is selected from the group consisting of poly(acrylic acid), poly(ethylene glycol), poly(2-hydroxyethyl methacrylate), poly(vinyl imidazole), poly(2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline), poly(vinylpyrolidone), cellulose, modified cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydrogels, PEG diacryalate, monoacrylate, and combinations thereof.

The low-surface-energy polymer and the hygroscopic material may be covalently connected, or are capable of being covalently connected, in a block copolymer. For example, a block copolymer may be a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

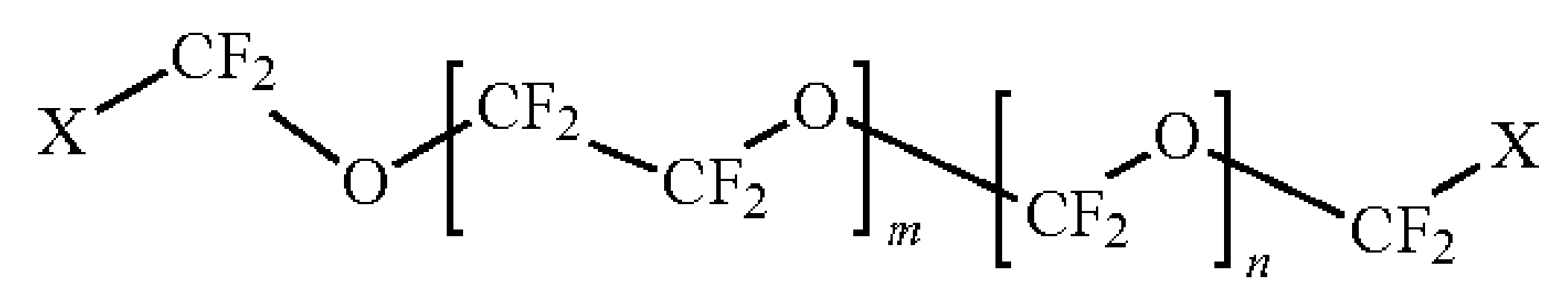
(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0, such as from about 0.1 to about 1.5.

In some embodiments, the fluoropolymers include a fluoropolymer having the structure:



wherein:

X=CH$_2$—(CH$_2$—CH$_2$—O)$_p$—OH wherein p=0 to 50;
m=1 to 100; and
n=1 to 100.

In some embodiments, the polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), poly(propylene glycol), poly(tetrahydrofuran), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly(hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof.

The low-surface-energy polymer and/or the hygroscopic material may be surface-treated, either prior to introduction into the precursor material or prior to conversion of the precursor material to the low-friction, low-adhesion material.

The precursor material may further contain one or more additional components selected from the group consisting of a particulate filler, a pigment, a dye, a plasticizer, a flame retardant, a flattening agent, and a substrate adhesion promoter. Alternatively, or additionally, such additional components may be introduced during the conversion of the precursor material to the low-friction, low-adhesion material, or to the low-friction, low-adhesion material after it is formed.

Specific particulate fillers include, for example, silica, alumina, silicates, talc, aluminosilicates, barium sulfate, mica, diatomite, calcium carbonate, calcium sulfate, carbon, wollastonite, and combinations thereof. The particulate fillers generally should be in the size range of about 5 nm to about 2 μm, such as about 20 nm to 100 nm.

The particulate fillers may be surface-modified with a compound selected from the group consisting of fatty acids, silanes, silicones, alkyl phosphonates, alkyl phosphonic acids, alkyl carboxylates, and combinations thereof. Optionally, the fillers may be surface-modified with a hydrophobic material, such as (but not limited to) an alkylsilane, a fluoroalkylsilane, and/or an alkyldisilazane (e.g., hexamethyldisilazane).

Any known methods to fabricate these materials or coatings may be employed. Notably, these materials or coatings may utilize synthesis methods that enable simultaneous deposition of components or precursor materials to reduce fabrication cost and time. In particular, these materials or coatings may be formed by a one-step process, in some embodiments. In other embodiments, these materials or coatings may be formed by a multiple-step process.

The low-friction, low-adhesion hydrophobic or hydrophilic material, in some embodiments, is formed from a precursor material (or combination of materials) that may be provided, obtained, or fabricated from starting components. The precursor material is capable of hardening or curing in some fashion, to form a substantially continuous matrix along with a plurality of inclusions, dispersed within the matrix. The precursor material may be a liquid; a multiphase liquid; a multiphase slurry, emulsion, or suspension; a gel; or a dissolved solid (in solvent), for example.

The low-surface-energy polymer and the hygroscopic material may be in the same phase or in different phases. In some embodiments, the low-surface-energy polymer is in liquid or dissolved form while the hygroscopic material is in dissolved-solid or suspended solid form. In some embodiments, the low-surface-energy polymer is dissolved-solid or suspended-solid form while the hygroscopic material is in liquid or dissolved form. In some embodiments, the low-surface-energy polymer and the hygroscopic material are both in liquid form. In some embodiments, the low-surface-energy polymer and the hygroscopic material are both in dissolved (solvent) form.

In some variations of the invention, a material or coating precursor is applied to a substrate (such as a surface of an automobile or aircraft) and allowed to react, cure, or harden to form a final coating, wherein the material, coating precursor, or final coating contains a segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein the fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(b) one or more second soft segments selected from polyesters or polyethers, wherein the polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) one or more isocyanate species, or a reacted form thereof, possessing an isocyanate functionality of 2 or greater; and

(d) one or more polyol or polyamine chain extenders or crosslinkers, or a reacted form thereof,

wherein the molar ratio of the second soft segments to the first soft segments is less than 2.0.

In some embodiments, the hygroscopic material is also hardenable, either alone or in combination with the low-surface-energy polymer. For instance, a low-surface-energy polymer and a hygroscopic polymer may form a high-molecular-weight block copolymerize and thus harden. In certain embodiments, the hygroscopic material assists in the curability (hardenability) of the low-surface-energy polymer.

In some embodiments, a precursor material is prepared and then dispensed (deposited) over an area of interest. Any known methods to deposit precursor materials may be employed. A fluid precursor material allows for convenient dispensing using spray coating or casting techniques over a large area, such as the scale of a vehicle or aircraft.

The fluid precursor material may be applied to a surface using any coating technique, such as (but not limited to) spray coating, dip coating, doctor-blade coating, spin coating, air knife coating, curtain coating, single and multilayer slide coating, gap coating, knife-over-roll coating, metering rod (Meyer bar) coating, reverse roll coating, rotary screen coating, extrusion coating, casting, or printing. Because relatively simple coating processes may be employed, rather than lithography or vacuum-based techniques, the fluid precursor material may be rapidly sprayed or cast in thin layers over large areas (such as multiple square meters).

When a solvent or carrier fluid is present in the fluid precursor material, the solvent or carrier fluid may include one or more compounds selected from the group consisting of water, alcohols (such as methanol, ethanol, isopropanol, or tert-butanol), ketones (such as acetone, methyl ethyl ketone, or methyl isobutyl ketone), hydrocarbons (e.g., toluene), acetates (such as tert-butyl acetate), acids (such as organic acids), bases, and any mixtures thereof. When a solvent or carrier fluid is present, it may be in a concentration of from about 10 wt % to about 99 wt % or higher, for example.

The precursor material may be converted to an intermediate material or the final material using any one or more of curing or other chemical reactions, or separations such as removal of solvent or carrier fluid, monomer, water, or vapor. Curing refers to toughening or hardening of a polymeric material by cross-linking of polymer chains, assisted by electromagnetic waves, electron beams, heat, and/or chemical additives. Chemical removal may be accomplished by heating/flashing, vacuum extraction, solvent extraction, centrifugation, etc. Physical transformations may also be involved to transfer precursor material into a mold, for example. Additives may be introduced during the hardening process, if desired, to adjust pH, stability, density, viscosity, color, or other properties, for functional, ornamental, safety, or other reasons.

The overall thickness of the final material or coating may be from about 1 μm to about 1 cm or more, such as about 10 μm, 20 μm, 25 μm, 30 μm, 40 μm, 50 μm, 75 μm, 100 μm, 500 μm, 1 mm, 1 cm, or 10 cm. Relatively thick coatings offer good durability and mechanical properties, such as impact resistance, while preferably being relatively lightweight.

EXAMPLES

Materials. Poly(ethylene glycol) (PEG) with molecular weight (M_n) of 3,400 g/mol, 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI), 1,4-butanediol (BD), and dibutyltin dilaurate (DBTDL) were purchased from Aldrich. Fluorolink D4000 and Fluorolink E10-H perfluoropolyether were purchased from Solvay Specialty Polymers. All chemicals were used as received without further purification.

Example A: Fluoropolymer Control

Flurolink D4000 perfluoropolyether (4 g) is charged to a vial followed by HMDI (0.786 g). A small PTFE-coated stir bar is introduced and the vial is placed in a 100° C. oil bath to stir. The reaction is vortexed aggressively after achieving a temperature of 100° C., and then left to stir for 1 hour. After this step, the resin is poured into a 3"×3" PTFE mold to flash off solvent and cure the film at room temperature overnight.

Example B: Perfluoropolyether/Poly(Ethylene Glycol) Block Copolymer

PEG (1.5 mmoles, 5.1 g) and HMDI (15 mmoles, 3.94 g) are added into a 3-neck flask equipped with a mechanical stirrer. The reaction flask is placed in a 100° C. oil bath. The reaction is carried out under argon. Once PEG is melted and dissolved in the HMDI, 10 μl of DBTDL is added to the mix. The reaction mixture is stirred at 100° C. for 1 hour. Fluorolink D4000 (1.5 mmoles, 6 g) is added and stirring is continued for another 1.75 hours. The reaction flask is removed from the 100° C. oil bath, and allowed to cool down before adding THF (10 ml) and BD (12 mmoles, 1.08 g) dissolved in THF (2 mL). The THF and BD are added to the viscous resin and vortexed to disperse and thin the overall mixture (precursor material).

The precursor material resin is then poured into a 3"×3" PTFE mold to flash off solvent and cure the precursor material film at room temperature overnight. The next day the film is placed in an 80° C. oven for 4 hours to complete the cure. The cured material is a perfluoropolyether/poly (ethylene glycol) block copolymer with a molar ratio of PEG to perfluoroether of 1.0.

Example B2: Perfluoropolyether/Poly(Ethylene Glycol) Block Copolymer

PEG (1.5 mmoles, 5.1 g) and HMDI (15 mmoles, 3.94 g) are added into a 3-neck flask equipped with a mechanical stirrer. The reaction flask is placed in a 100° C. oil bath. Once PEG melts and dissolves in the HMDI, 10 μl of DBTDL is added to the mix. The reaction mixture is stirred at 100° C. for 1 hour. Fluorolink D4000 (1.5 mmoles, 6 g) is added and stirring is continued for another 1.75 hours. The reaction flask is removed from the 100° C. oil bath, and allowed to cool down before adding THF (10 ml), BYK-LP X 22325 and vortexed to disperse silica in the mixture. 1,4-Butanediol (12 mmoles, 0.161 g) dissolved in THF (2 mL) is added to the mixture and vortexed.

The precursor material resin is then poured into a 3"×3" PTFE mold to flash off solvent and cure the precursor material film at room temperature overnight. The next day the film is placed in an 80° C. oven for 4 hours to complete the cure. The cured material is a perfluoropolyether/poly (ethylene glycol) block copolymer with a molar ratio of PEG to perfluoroether of 1.0, further comprising a silica filler.

Example C: Perfluoropolyether/Poly(Ethylene Glycol) Block Copolymer

The procedure described in Example B is followed, except that the cured material is a perfluoropolyether/poly (ethylene glycol) block copolymer with a molar ratio of PEG to perfluoroether of 1.33.

Example D: Perfluoropolyether/Poly(Ethylene Glycol) Block Copolymer

PEG (2 mmoles, 6.8 g) and HMDI (12.8 mmoles, 3.36 g) are added into a 3-neck flask equipped with a mechanical stirrer. The reaction flask is placed in a 100° C. oil bath. The reaction is carried out under argon. Once PEG is melted and dissolved in the HMDI, 10 μl of DBTDL is added to the mix. The reaction mixture is stirred at 100° C. for 1 hour. Fluorolink E10-H (2 mmoles, 3 g) is added and stirring continues another 1.75 hours. The reaction flask is removed from 100° C. oil bath, and allowed to cool down before adding THF (8 mL) and BD (8.8 mmoles, 0.8 g) dissolved in THF (2 mL).

The precursor material resin is then poured into a 3"×3" PTFE mold to flash off solvent and cure the precursor material film at room temperature overnight. The next day the film is placed in an 80° C. oven for 4 hours to complete the cure. The cured material is a perfluoropolyether/poly (ethylene glycol) block copolymer with a molar ratio of PEG to perfluoroether of 1.0.

Comparative Example E: Perfluoropolyether/Poly(Ethylene Glycol) Block Copolymer with High PEG Fraction

PEG (3 mmoles, 10.2 g) and HMDI (20 mmoles, 5.25 g) are added into a 3-neck flask equipped with a mechanical stirrer. The reaction flask is placed in a 100° C. oil bath. The reaction is carried out under argon. Once PEG is melted and dissolved in the HMDI, 12 μl of DBTDL is added to the mix. The reaction mixture is stirred at 100° C. for 1 hour. Fluorolink D4000 (1 mmoles, 4 g) is added and stirring continues for another 2 hours. The reaction flask is removed from 100° C. oil bath, and allowed to cool down before adding THF (10 mL) and BD (16 mmoles, 1.44 g) dissolved in THF (3 mL).

The precursor material resin is then poured into a 3"×3" PTFE mold to flash off solvent and cure the precursor material film at room temperature overnight. The next day the film is placed in an 80° C. oven for 4 hours to complete the cure. The cured material is a perfluoropolyether/poly (ethylene glycol) block copolymer with a molar ratio of PEG to perfluoroether of 3.0.

Comparative Example F: Perfluoropolyether/Poly(Ethylene Glycol) Block Copolymer with High PEG Fraction

PEG (3 mmoles, 10.2 g) and HMDI (12.8 mmoles, 3.36 g) are added into a 3-neck flask equipped with a mechanical stirrer. The reaction flask is placed in a 100° C. oil bath. The reaction is carried out under argon. Once PEG is melted and dissolved in the HMDI, 12 μl of DBTDL is added to the mix. The reaction mixture is stirred at 100° C. for 1 hour. Fluorolink E10-H (1 mmoles, 1.5 g) is added and stirring continues for another 2 hours. The reaction flask is removed from 100° C. oil bath, and allowed to cool down before adding THF (8 mL) and BD (8.8 mmoles, 0.8 g) dissolved in THF (2 mL).

The precursor material resin is then poured into a 3"×3" PTFE mold to flash off solvent and cure the precursor material film at room temperature overnight. The next day the film is placed in an 80° C. oven for 4 hours to complete the cure. The cured material is a perfluoropolyether/poly (ethylene glycol) block copolymer with a molar ratio of PEG to perfluoroether of 3.0.

Friction Testing.

The change in friction in response to humidity is tested by equilibrating the samples of Examples A, B, C, D, E, and F at ambient (40-55%) relative humidity or 90% relative humidity in a humidity-controlled chamber. Then the samples are placed on a variable-angle stage and the angle is increased until a 5-gram cylindrical mass slides along the sample surface. The sliding angle is used to determine the friction constant (coefficient of friction). The friction change is shown for the samples of Examples A-F in the table of FIG. **3**. While the friction coefficient increases with increased humidity, the final result is still a smooth low-friction coating.

Ice Formation Testing.

The kinetic delay of freezing is measured by placing three 50 μL drops of deionized water on a surface held at −10° C. with a thermoelectric cooler. The time for ice to initially form in the droplets is measured. The kinetic delay of freezing is shown for the samples of Examples A, B, C, D, E, and F and Al control in the table of FIG. **3**. A bare aluminum (Al) surface has an ice formation delay of 0.2±0.1 minutes. The Example A fluoropolymer control demonstrates an ice formation delay of 1.3 min±0.9 min.

The surprisingly long ice formation delay of materials of Examples C, D, and E may be due to the material trapping water at the surface. Without being limited by theory, it is believed that this trapped layer of water cannot freeze because the hygroscopic domains inhibit the crystallization reaction mechanisms in the surface water. Any droplet of water on the surface sees liquid water instead of a coating on the surface; ice nucleation is confined to the homogeneous nucleation regime that is kinetically much slower than heterogeneous nucleation.

Samples from Examples B, C, and D show extended freezing delays. The Comparative Examples E and F, with 3:1 molar ratio of PEG to fluoropolymer, are characterized by freezing delays that are notably shorter than the samples of Examples B, C, and D. Also, due to higher PEG content in Comparative Examples E and F, elevated humidity creates an undesirably tacky surface that does not allow for easy sliding on the coating surface.

Vehicle-based cameras for surrounding awareness will require lens coatings that will inhibit soiling in order to function. Once soiled, the camera will lose effectiveness and eventually cease functioning. The coatings/surfaces described herein may be used as camera lens coatings, and may be transparent.

Aircraft lose efficiency from disruption of laminar flow when insect and particulate debris collect on the aircraft wings. This invention provides materials that reduce the adhesion of insect and particulate debris on aircraft surfaces, while simultaneously inhibiting the formation of ice.

Other practical applications for the present invention include, but are not limited to, vehicle windows, optical lenses, filters, instruments, sensors, eyeglasses, cameras, satellites, and weapon systems. For example, automotive applications can utilize these coatings to prevent the formation of ice or debris on back-up camera lenses or back-up sensors. The principles taught herein may also be applied to self-cleaning materials, anti-adhesive coatings, corrosion-free coatings, etc.

In this detailed description, reference has been made to multiple embodiments and to the accompanying drawings in which are shown by way of illustration specific exemplary embodiments of the invention. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that modifications to the various disclosed embodiments may be made by a skilled artisan.

Where methods and steps described above indicate certain events occurring in certain order, those of ordinary skill in the art will recognize that the ordering of certain steps may be modified and that such modifications are in accordance with the variations of the invention. Additionally, certain steps may be performed concurrently in a parallel process when possible, as well as performed sequentially.

All publications, patents, and patent applications cited in this specification are herein incorporated by reference in their entirety as if each publication, patent, or patent application were specifically and individually put forth herein.

The embodiments, variations, and figures described above should provide an indication of the utility and versatility of the present invention. Other embodiments that do not provide all of the features and advantages set forth herein may also be utilized, without departing from the spirit and scope of the present invention. Such modifications and variations are considered to be within the scope of the invention defined by the claims.

What is claimed is:

1. A segmented copolymer composition comprising:

(a) one or more first soft segments selected from fluoropolymers having an average molecular weight from about 500 g/mol to about 10,000 g/mol, wherein said fluoropolymers contain an oxygen atom connected to two alkyl or aryl groups, wherein at least one hydrogen atom of said alkyl or aryl group is replaced by a fluorine atom, and wherein said fluoropolymers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(b) one or more second soft segments selected from polyesters or polyethers, wherein said polyesters or polyethers are selected from the group consisting of poly(oxymethylene), poly(ethylene glycol), poly(propylene glycol), poly(glycolic acid), poly(caprolactone), poly(ethylene adipate), poly(hydroxybutyrate), poly(hydroxyalkanoate), and combinations thereof, and wherein said polyesters or polyethers are (α,ω)-hydroxyl-terminated and/or (α,ω)-amine-terminated;

(c) a hard segment containing a reacted form of one or more isocyanate species possessing an isocyanate functionality of 2 or greater; and

(d) in said hard segment, a reacted form of one or more polyol or polyamine chain extenders or crosslinkers,

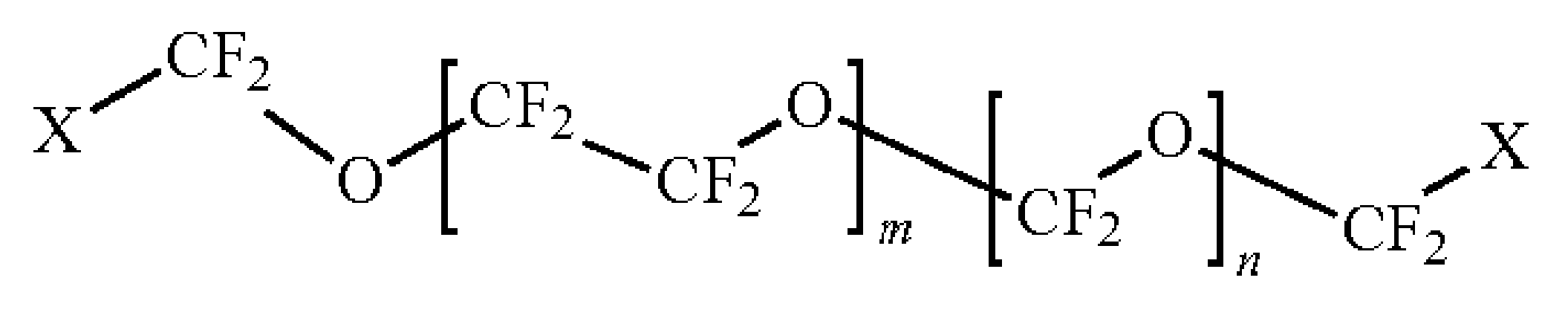
wherein the molar ratio of said second soft segments to said first soft segments is less than 2.0, and

wherein said first soft segments, said second soft segments, and said hard segments are microphase-separated.

2. The segmented copolymer composition of claim **1**, wherein said molar ratio of said second soft segments to said first soft segments is from about 0.1 to about 1.5.

3. The segmented copolymer composition of claim **1**, wherein said fluoropolymers are selected from the group consisting of perfluoropolyethers, polyfluoroacrylates, polyfluorosiloxanes, and combinations thereof.

4. The segmented copolymer composition of claim **1**, wherein said fluoropolymers include a fluoropolymer having the structure:



wherein:

X=CH_2—$(CH_2$—CH_2—$O)_p$—OH wherein p=0 to 50;

m=1 to 100; and

n=1 to 100.

5. The segmented copolymer composition of claim **1**, wherein said isocyanate species is selected from the group consisting of 4,4'-methylenebis(cyclohexyl isocyanate), hexamethylene diisocyanate, cycloalkyl-based diisocyanates, tolylene-2,4-diisocyanate, 4,4'-methylenebis(phenyl isocyanate), isophorone diisocyanate, and combinations or derivatives thereof.

6. The segmented copolymer composition of claim **1**, wherein at least one polyol or polyamine chain extender or crosslinker of said one or more polyol or polyamine chain extenders or crosslinkers possesses a functionality of 2 or greater.

7. The segmented copolymer composition of claim **6**, wherein said at least one polyol or polyamine chain extender or crosslinker is selected from the group consisting of 1,3-butanediol,1,1,4-butanediol, 1,3-propanediol, 1,2-ethanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, neopentyl glycol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, ethanol amine, diethanol amine, methyldiethanolamine, phenyldiethanolamine, glycerol, trimethylolpropane, 1,2,6-hexanetriol, triethanolamine, pentaerythritol, ethylenediamine, 1,3-propanediamine, 1,4-buatendiamine, diethyltoluenediamine, dimethylthiotoluenediamine, isophoronediamine, diaminocyclohexane, N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine, and homologues, derivatives, or combinations thereof.

8. The segmented copolymer composition of claim **1**, wherein said hard segment is present in an amount from about 5 wt % to about 60 wt %, based on total weight of said composition.

9. The segmented copolymer composition of claim **1**, wherein said segmented copolymer composition is present in a coating.

10. The segmented copolymer composition of claim **9**, wherein said coating is characterized by a coefficient of friction, measured at 90% relative humidity, less than 0.7.

11. The segmented copolymer composition of claim **9**, wherein said coating is characterized by an average kinetic delay of surface ice formation of at least 5 minutes at −10° C.

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